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Ultrafine microstructures make superhard materials harder

As advanced tool materials, diamond and cubic boron nitride (cBN) play a vital role in the modern processing industry. Nonetheless, each material has some intrinsic drawbacks, such as the inferior thermal stability of diamond and the relatively low hardness and toughness of cBN. A simultaneous improvement in the hardness, toughness, and thermal stability of these materials has long been desired in the scientific and industry communities. The identification of a synthetic material that is harder than natural diamond has always been a human aspiration. After years of effort, however, scientists are becoming pessimistic about the realization of such a dream. For example, Chaudrhi *et al.* from the Cavendish Laboratory of Cambridge University claimed the following in his paper titled, *Harder than diamond? Just fiction* (*Nat Mater*, 2005, 4: 4).

Researchers in Prof. Yongjun Tian's group (Yanshan University) carried out a systematic study in response to these challenges. They established a theoretical hardness model for polycrystalline polar covalent materials *(Int J Refract Met Hard Mater*, 2012, 33: 93), and revealed that the hardness can be enhanced by decreasing the characteristic microstructure size because of the dual contributions from the Hall-Petch and quantum confinement effects. However, to achieve a characteristic microstructural size for diamond and cBN below 10 nm is a technical challenge, as indicated by numerous previous attempts. Through the structural transitions of onion-structured precursors under high pressure and high temperature, Tian *et al*. synthesized nanotwinned cBN (nt-cBN) [1] and nanotwinned diamond (nt-diamond) [2] materials, with a remarkable average twin thickness of 3.8 nm and 5 nm, respectively. The nt-cBN had a Vickers hardness of 108 GPa, which is even harder than synthetic diamond. The fracture toughness increased to 12.7 MPa $m^{0.5}$, which is 4.5 times that of a cBN single crystal. The oxidation temperature of nt-diamond in air is more than 200 °C higher than that of natural diamond and it has a Vickers hardness of up to 200 GPa (as shown in Figure 1). These results turn fiction into reality. The successful syntheses of nt-cBN and nt-diamond verify their proposed hardness model and realize simultaneous improvement in hardness, toughness and thermal stability. This provides a new principle and presents a technique to obtain high-performance superhard materials. The exploitation of this type of ultrahard material in industry will raise machining efficiency, processing methods and equipment technology to a new level.

Another point that should be mentioned is that Tian *et al*. clarified the principle of hardness measurements for materials harder than diamond. By analyzing the stress states in the diamond indenter and the tested sample during the indentation process, they proposed a criterion for the reliable measurement of materials hardness [2, 3]. The indentation hardness can be measured reliably as long as the sample shear strength is smaller than the compressive strength of the indenter diamond. This criterion corrects a long-term misconception in hardness measurements of superhard materials (*Nat Mater*, 2004, 3: 576).

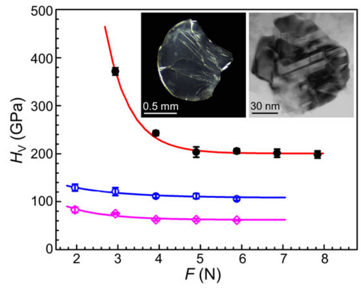

Figure 1 Vickers hardness, H_V, of nt-diamond (red line) and natural diamond single crystal (blue line: {110} face; and pink line: {111} face) as a function of applied load, F. The left inset shows a photograph of a transparent bulk nt-diamond sample synthesized at 20 GPa and 2000 °C. The right inset shows a typical TEM image of the nanotwinned microstructure in an nt-diamond (image credit: XU Bo, HU WenTao and HUANG Quan from Yanshan University).

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1 Tian Y, Xu B, Yu D, Ma Y, Wang Y, Jiang Y, Hu W, Tang C, Gao Y, Luo K, Zhao Z, Wang L-M, Wen B, He J, Liu Z. Ultrahard nanotwinned cubic boron nitride. *Nature*, 2013, 493: 385–388
2 Huang Q, Yu D, Xu B, Hu W, Ma Y, Wang Y, Zhao Z, Wen B, He J, Liu Z, Tian Y. Nanotwinned diamond with unprecedented hardness and stability. *Nature*, 2014, 510: 250–253
3 Tian Y, Xu B, Yu D, Ma Y, Wang Y, Jiang Y, Hu W, Tang C, Gao Y, Luo K, Zhao Z, Wang L-M, Wen B, He J, Liu Z. Controversy about ultrahard nanotwinned cBN reply. *Nature*, 2013, 502: E2-3